

12

# EUROPEAN PATENT APPLICATION

21 Application number: 84306505.3

51 Int. Cl.<sup>4</sup>: H 01 L 21/203  
 H 01 L 31/18

22 Date of filing: 24.09.84

30 Priority: 26.09.83 US 535901

43 Date of publication of application:  
 02.05.85 Bulletin 85/18

84 Designated Contracting States:  
 DE FR GB IT

71 Applicant: Exxon Research and Engineering Company  
 P.O.Box 390 180 Park Avenue  
 Florham Park New Jersey 07932(US)

72 Inventor: Maruska, Herbert Paul  
 R.D. 1, Box 333  
 Annandale New Jersey 08801(US)

72 Inventor: Moustakas, Theodora Demetri  
 7 Cambridge Drive  
 Annandale New Jersey 08801(US)

74 Representative: Field, Roger Norton et al,  
 ESSO Engineering (Europe) Ltd. Patents & Licences Apex  
 Tower High Street  
 New Malden Surrey KT3 4DJ(GB)

54 A method for sputtering a pin or nip amorphous silicon semi-conductor device having partially crystallised P and N-layers.

57 A high efficiency amorphous silicon PIN or NIP semicon-  
 ductor device having partially crystallised (microcrystalline) P  
 and N layers is constructed by the sequential sputtering of N,  
 I and P layers and at least one semi-transparent ohmic  
 electrode. The method of construction produces a PIN or NIP  
 device, exhibiting enhanced electrical and optical properties,  
 improved physical integrity, and facilitates the preparation in  
 a singular vacuum system and vacuum pump down procedure.

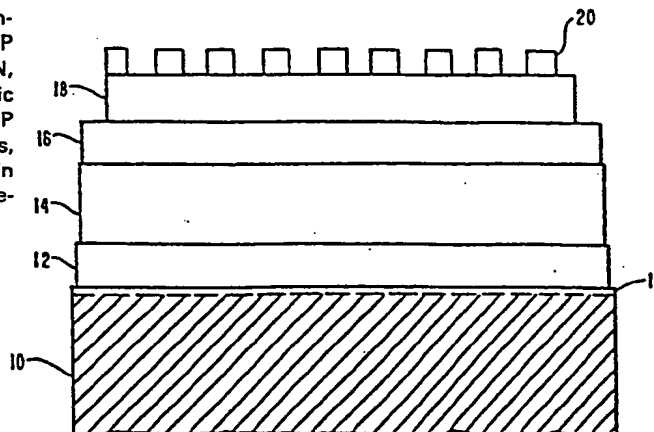


FIG. 1

1

2           The present invention relates to hydro-  
3 genated amorphous silicon and more particularly to a  
4 method for reactively sputtering a PIN amorphous sili-  
5 con semiconductor device having partially crystallized  
6 P and N layers.

7           Amorphous silicon has been used in a number  
8 of semiconductor devices, the most promising of which  
9 is the PIN structure. Such devices were first fabri-  
10 cated by the method of glow discharge decomposition of  
11 silane and described in a technical publication by  
12 D. E. Carlson, J. Non-Crystalline, 35-36, (1980)  
13 p. 707. The P and N layers in this method are  
14 deposited by mixing approximately 1 to 2% of B<sub>2</sub>H<sub>6</sub> or  
15 PH<sub>3</sub> in the silane discharge. The principal deficiency  
16 of this device, as noted by Carlson, is that the P-  
17 layer which forms the major semiconductor junction  
18 with the I-layer, is both poorly conductive and  
19 absorbs the incident light energy without signifi-  
20 cantly contributing to the collection of photogener-  
21 ated charge carriers in the device. Because the  
22 N-layer absorbs much less light than the P-layer,  
23 Carlson has shown that illumination from the N-side  
24 leads to higher solar cell efficiency.

25           A further improvement to the efficiency of  
26 this device has been described in a technical publica-  
27 tion by Y. Uchida et al., Japanese Journal of Applied  
28 Physics, 21, (1982) p. L586. These authors fabricated  
29 the N-layer by glow discharge decomposition of a mix-  
30 ture of SiH<sub>4</sub>-H<sub>2</sub>-PH<sub>3</sub> and high power in the discharge.  
31 Under these conditions, they claim that the N-layer is

1 partially crystallized (microcrystalline) and there-  
2 fore it is both highly conductive and highly trans-  
3 parent in the visible part of the spectrum. This type  
4 of N-layer is ideal as a "window" material and leads  
5 to a 13% improvement in the short-circuit current of  
6 the solar cell. The devices reported by Uchida have  
7 the configuration stainless steel/PIN/ITO with the P  
8 and I-layers being amorphous and the N-layer being  
9 microcrystalline.

10 PIN semiconductor devices have also been  
11 fabricated by the method of reactive sputtering and  
12 described in a technical publication by T. D.  
13 Moustakas and R. Friedman, Appl. Phys. Lett. 40,  
14 (1982) p. 515. The I-layer of these devices was fabri-  
15 cated by sputtering from an undoped silicon target in  
16 an atmosphere of Argon containing 10-20% H<sub>2</sub>. The P and  
17 N-layers were fabricated by adding approximately 0.1  
18 to 1% of B<sub>2</sub>H<sub>6</sub> or PH<sub>3</sub> in the Ar-H<sub>2</sub> discharge. The  
19 hydrogen content for the "window" (P-layer) was  
20 increased to approximately 20 to 40% in order to im-  
21 prove its transparency to visible light. All three  
22 layers (P, I, N) if this device are amorphous.

23 In view of the improvements of the solar  
24 cell efficiency of PIN devices produced by glow dis-  
25 charge decomposition of silane employing a micro-  
26 crystalline N-contact as a "window" layer, it is  
27 important to fabricate such devices by the method of  
28 RF sputtering.

29

30 The invention is directed to a method for  
31 depositing by RF sputtering an amorphous PIN Semi-  
32 conductor device, having the "window" (P or N) or both

1 contacts deposited under conditions which lead to  
2 partially crystallized (microcrystalline) material.  
3 The method of the present invention shall be illus-  
4 trated and described with respect to a PIN device. It  
5 is to be understood, however, that the method of the  
6 present invention applies equally well to a NIP  
7 device.

8           A microcrystalline N-layer is deposited by  
9 RF sputtering from an undoped silicon target in an  
10 atmosphere containing hydrogen, argon and phosphine at  
11 a total pressure larger than 20 mTorr with  $H_2/Ar \gg 1$   
12 and phosphine content approximately 0.1 to 1 vol % of the  
13 argon content. The power in the discharge is adjusted  
14 to lead to DC bias target voltage of between -800 to  
15 -2000 volts and the substrate temperature to between  
16 200 to 400°C. An intrinsic layer is also reactively  
17 sputtered from an undoped target in an atmosphere of 5  
18 to 15 mTorr of argon containing 10 to 20 vol % hydrogen.  
19 The target voltage and the substrate temperature are  
20 the same as during the deposition of the N-layer. This  
21 I-layer is amorphous. A microcrystalline P-layer is  
22 reactively sputtered from an undoped silicon target in  
23 an atmosphere containing hydrogen, argon and diborane  
24 at a total pressure larger than 20 mTorr with  $H_2/Ar \gg 1$   
25 and diborane content approximately 0.1 to 1 vol % of the  
26 argon content. The target voltage and the substrate  
27 temperature vary in the same range as those of the N  
28 and I-layers. The contact (P or N) which is deposited  
29 on the top of the I-layer is preferably deposited at  
30 lower target voltage ( -800 volts) in order to avoid  
31 surface damage of the I-layer. [The three layers are  
32 deposited sequentially in three interlocked chambers  
33 in order to avoid cross contamination between the  
34 layers. If they are deposited in the same chamber the  
35 chamber has to be purged and sputtercleaned between

1 the first doped and the intrinsic layer.] Transparent  
2 electrodes and metallic grids are also sputter de-  
3 posited which permits the entire deposition to be  
4 accomplished in one sputtering apparatus and in one  
5 vacuum pump-down. When the P and N layers are fabri-  
6 cated in microcrystalline form, the PIN solar cells  
7 have an open circuit voltage of about 0.1 to 0.20 V  
8 higher than entirely amorphous PIN solar cells and 10  
9 to 20% higher short circuit current due to the better  
10 blue response of these solar cells.

11 In the drawings:

12 Figure 1 shows a greatly enlarged side view  
13 of a semi-conductor device constructed in accordance  
14 with the teaching of the present invention.

15 Figure 2 shows the I-V characteristics of a  
16 sputtered PIN solar cell having microcrystalline P and  
17 N layers.

18 Figure 3 shows the increase in the collec-  
19 tion efficiency in the blue portion of the spectrum of  
20 a PIN Cell by using a microcrystalline P-layer for the  
21 front contact and a microcrystalline N-layer as the  
22 rear contact compared to one having amorphous P-layer  
23 and N-layer.

24

25 The sputtered amorphous silicon PIN device  
26 of the present invention, as illustrated in Figure 1,  
27 includes a substrate 10 which generally comprises a  
28 physically supportive substrate for the overlying  
29 sputter deposited layers. Substrate 10 includes a

1 major area coating surface which is substantially free  
2 from voids or protrusions of the order (in size) of  
3 the thickness of the overlying layers to avoid pin  
4 holes therethrough.

5           In one embodiment, substrate 10 may comprise  
6 a non-electroconductive material such as glass or  
7 ceramic for which an overlying layer of an electro-  
8 conductive material 11 is required. Alternately, sub-  
9 state 10 may comprise a metal concurrently serving as  
10 a supportive substrate and an electrode contact to the  
11 overlying layers. In either instance, the coating  
12 surface of the substrate is thoroughly cleaned to  
13 remove unwanted contamination of the coating surface.  
14 In a preferred embodiment, electrode 10 comprises a  
15 metal known to form an ohmic contact to N-doped sili-  
16 con such as molybdenum or stainless steel for example.  
17 In the case where substrate 10 comprises a nonelectro-  
18 conductive material it is preferred that layer 11  
19 comprise a layer of metal known to form an ohmic con-  
20 tact to N-doped microcrystalline silicon; examples are  
21 molybdenum or chromium thin films of approximately  
22 1,000 to 2,000 Å thick or a transparent conductive  
23 oxide such as indium tin oxide (ITO),  $\text{SnO}_2$  or cadmium stannate  
24 approximately 1000 Å thick.

25           The substrates are fastened to the anode  
26 electrode of a conventional RF diode sputtering unit  
27 which is adapted to provide controlled partial pres-  
28 sures of hydrogen, argon, phosphine and diborane as  
29 detailed hereinafter. The term secured is intended in  
30 this application to mean both the physical securing of  
31 the substrate to the anode electrode and more impor-  
32 tantly the electrical contacting of the conducting  
33 coating surface to the anode electrode. In this manner  
34 the coating surface is maintained at the approximate

- 6 -

1 electrical potential of the anode electrode. The anode  
2 electrode is either electrically grounded or supplied  
3 with a positive or negative bias of approximately  $\pm 50$   
4 volts. The sputtering system is further adapted to  
5 provide for controlled temperature heating of the  
6 substrates. The deposition temperature as recited  
7 hereinafter is measured by a thermocouple embedded in  
8 the anode electrode.

9           It is to be recognized that the temperatures  
10 recited hereinafter are measured accordingly and the  
11 actual temperature of the depositing film may differ.

12           The sputtering system is evacuated to a base  
13 pressure of about  $1 \times 10^{-7}$  Torr by conventional  
14 mechanical and turbomolecular pumping means. An  
15 N-layer of hydrogenated microcrystalline silicon, 12,  
16 is sputter deposited by first heating substrate to a  
17 monitored temperature ranging from about  $200^{\circ}\text{C}$  to  
18 about  $400^{\circ}\text{C}$ . A sputtering target comprising a poly-c-  
19 rystalline undoped silicon disc about 5" in diameter  
20 is secured to the cathode electrode being located  
21 about 4.5 cm from the substrate platform (anode elec-  
22 trode). Consistent with the condition  $\text{H}_2/\text{Ar} \gg 1$  and  
23 total pressure  $\geq 20$  mTorr, as described above, the  
24 sputtering atmosphere comprises a partial pressure of  
25 hydrogen ranging from about 20 mTorr to about 80 mTorr  
26 and argon ranging from about 3 mTorr to about 10  
27 mTorr. For the best microcrystalline material, a pre-  
28 ferred combination of parameters should be  $\text{H}_2/\text{Ar} \geq 10$   
29 and  $\text{H}_2 + \text{Ar} \geq 40$  mTorr. To dope the hydrogenated  
30 microcrystalline silicon layer N an amount of phos-  
31 phine ( $\text{PH}_3$ ) is added to the partial pressures of hy-  
32 drogen and argon. In one embodiment, the argon source  
33 contains 0.2 - 1 atomic % of phosphine. The sputtering  
34 is accomplished at an RF power of about 100 to 200

- 7 -

1 watts resulting in an induced DC bias of about -800 to  
2 -2000 volts relative to the electrically grounded  
3 substrate platform (anode). The deposition rate of the  
4 films depends on the relative amounts of  $H_2$  to Ar in  
5 the discharge. These conditions lead to deposition  
6 rates between 10 to 40 Å/sec. These lower deposition  
7 rates of the microcrystalline material as compared to  
8 amorphous material are caused by the higher concentra-  
9 tion of  $H_2$  which leads to the etching of the deposited  
10 film and thus competes with the deposition process of  
11 silicon. The sputtered deposition continues for a time  
12 ranging from a minimum of 2.5 min. to about 10 mins.  
13 resulting in a thickness of N-layer, 12, ranging from  
14 about 100 angstroms to about 400 angstroms. Alterna-  
15 tively, the N layer can be produced in a graded form  
16 extending 500 to 1000 Å. This can be accomplished by  
17 progressively reducing the amount of  $PH_3$  in the disch-  
18 arge. The substrate heating described heretofore con-  
19 tinues throughout the deposition to maintain the moni-  
20 tored substrate temperature within the indicated  
21 range. This results in a proper level of hydrogenation  
22 of the depositing microcrystalline silicon which was  
23 found to be about 3-4% by unfarred spectroscopy.

24       An intrinsic layer of hydrogenated silicon  
25 14 is sputter deposited from an undoped silicon target  
26 in an atmosphere containing pure argon and hydrogen.  
27 This layer 14 is amorphous. The sputtering atmosphere  
28 for depositing the intrinsic layer ranges from about 3  
29 mTorr to about 15 mTorr of pure argon and from about  
30 0.3 mTorr to about 1.5 mTorr of hydrogen. The RF power  
31 conditions, cathode and anode configuration, and sub-  
32 strate temperature are substantially identical to that  
33 described for the sputter deposition of the N-layer.  
34 Under these conditions, a layer of intrinsic amorphous



- 8 -

1 silicon ranging from about 0.2 microns to about 1.5  
2 microns in thickness is deposited at a rate ranging  
3 from 60A/min to 1000A/min.

4           A P-doped layer of hydrogenated microcrys-  
5 talline silicon 16 is sputtered deposited from an  
6 atmosphere of argon, hydrogen and diborane. Consistent  
7 with the condition  $H_2/Ar \gg 1$  and total pressure  $> 20$   
8 mTorr, as described above, a sputtering atmosphere  
9 comprising argon and hydrogen having partial pressures  
10 ranging from about 3 mTorr to about 10 mTorr and about  
11 20 mTorr to about 80 mTorr respectively, includes a  
12 level of diborane dopant sufficient to dope the micro-  
13 crystalline silicon P-type. For the best microcrys-  
14 talline material, a preferred combination of param-  
15 eters should be  $H_2/Ar \geq 10$  and  $H_2 + Ar \geq 40$  mTorr. In  
16 one embodiment, the argon source contains about 0.2 to  
17 1 atomic % of diborane ( $B_2H_6$ ). The sputtering power  
18 conditions, monitored substrate temperature ranges,  
19 and configuration of the anode and cathode electrodes  
20 are substantially identical to those described for the  
21 deposition of the N and I layers. The deposition rate  
22 of the film depends on the relative amounts of H and  
23 Ar in the discharge. These conditions lead to deposi-  
24 tion rates of 10A/min to 40A/min. The thickness of the  
25 P-layer, as compared to the thickness of the intrinsic  
26 and N-doped layers is smaller, ranging from about 80  
27 to about 150 angstroms. As presently understood, the  
28 P-layer functions to form a potential barrier with the  
29 I-layer. The P and N layers fabricated according to  
30 the descriptions given above were found by X-ray and  
31 Raman spectroscopy to be partially crystallized with  
32 crystallite size of 50-60A. Furthermore, the index of  
33 refraction of these P and N layers in the visible  
34 spectral region are about 3.0 while that of the amor-  
35 phous silicon is about 4.0. The P and N layers were

1 also found to be about one half an order of magnitude  
2 less absorbing to visible light than the corresponding  
3 amorphous layers. In addition, they have conductivi-  
4 ties between 1 and 10 ( $\Omega\text{cm}$ )<sup>-1</sup> while the corresponding  
5 amorphous P and N layers have conductivities of 10<sup>-2</sup>  
6 to 10<sup>-3</sup> ( $\Omega\text{cm}$ )<sup>-1</sup>. A current collection electrode 18,  
7 comprises an electroconductive material which is semi-  
8 transparent in the spectral region ranging from about  
9 3,500 angstroms to about 7,000 angstroms, which con-  
10 stitutes the principal absorption region of the under-  
11 lying amorphous silicon film layers. Further, elec-  
12 trode 18 must form a substantially ohmic contact to  
13 the contiguous P-doped microcrystalline silicon. In  
14 one embodiment, electrode 18 may comprise a semi-  
15 transparent conductive oxide such as indium tin oxide,  
16 tin oxide or cadmium stannate. In such an embodiment,  
17 the thickness of the conductive oxide may be tailored  
18 to provide an anti-reflection coating to the underly-  
19 ing amorphous silicon surface. These conductive oxides  
20 are deposited by RF sputtering from corresponding  
21 targets. It is desirable that the oxide be deposited  
22 on the solar cell at temperatures between 250 and  
23 300°C to anneal any induced sputtering damage on the  
24 solar cell and to improve the sheet resistance which  
25 was found to be about 50 $\Omega/\square$ . The index of refraction of  
26 these oxides is about 2 to 2.2. Therefore, the index  
27 of refraction of the P and N layers of about 3 is an  
28 intermediate value between that of the oxide and that  
29 of the I layers. This gradual transition of the in-  
30 dices of refraction is desirable for better collection  
31 of light. In an alternative embodiment, electrode 18  
32 may comprise a relatively thin metallic layer, also  
33 being semitransparent and forming an ohmic contact to  
34 P-doped microcrystalline silicon. An example is plat-  
35 inum.

1           To further assist in the collection of  
2 current generated by the photovoltaic device, a grid  
3 electrode 20 may be patterned on the surface of elec-  
4 trode 18. The electroconductive grid, generally con-  
5 figured to minimize the area of coverage and concur-  
6 rently minimize the series resistance of the photo-  
7 voltaic cell, may be constructed by several alternative  
8 techniques well known in the art.

9           Those skilled in the art recognize that the  
10 use of a glass or other similarly transparent sub-  
11 strate 10, having an transparent electroconductive  
12 layer 11 (e.g. ITO or  $\text{SnO}_2$ ), permits illumination of  
13 the device through the substrate. Furthermore, the  
14 deposition sequence of P and N layers may be reversed  
15 to deposit a layer of P microcrystalline silicon onto  
16 an ITO coated substrate, having the intrinsic and N  
17 layers deposited thereupon.

18           It is to be recognized that the several  
19 layers comprising the photovoltaic device described  
20 heretofore, may be accomplished by sputtering tech-  
21 niques facilitating the construction of this device in  
22 a singular vacuum sputtering unit and in a singular  
23 vacuum pump down. It should further be recognized that  
24 the sputtering techniques used in the construction of  
25 a photovoltaic device of the present invention result  
26 in enhanced physical integrity and adherence of the  
27 deposited films. The method manifests in an ability to  
28 sputter deposit a layer of semi-transparent conductive  
29 oxides such as indium tin oxide onto a relatively thin  
30 P doped layer, 16, without deteriorating the junction  
31 forming characteristics of the underlying silicon  
32 layers. Essentially the cell can be illuminated either

1 from the substrate side or the side opposite the sub-  
2 strate because of the superior properties of the  
3 sputtered microcrystalline N and P layers.

#### 4 EXAMPLE

5           Figure 2 shows the I-V characteristics of a  
6 sputtered amorphous silicon PIN solar cell structures  
7 employing microcrystalline P and N layers. Note that  
8 the short circuit current in this device is  $13\text{mA}/\text{cm}^2$   
9 and the open circuit voltage is 0.86 volts. The sub-  
10 strate in this structure is mirror polished stainless  
11 steel. This substrate was ultrasonically cleaned and  
12 degreased before it was fastened to the anode elec-  
13 trode of the previously described diode sputtering  
14 unit. The vacuum chamber was evacuated to a base pres-  
15 sure of  $1 \times 10^{-7}$  Torr and the substrate was heated to  
16  $325^\circ\text{C}$ . The three active layers of the device were  
17 deposited under the conditions and order described  
18 below:

19           The partially crystallized N-layer was depo-  
20 sited in an atmosphere of 40 mTorr of  $\text{H}_2 + \text{Ar} + \text{PH}_3$ .  
21 The partial pressures of these gases were 36 mTorr of  
22 hydrogen and 4 mTorr of argon. The phosphine was con-  
23 tained in the cylinder of argon at a concentration of  
24 0.2 atomic %. Therefore, during the deposition of this  
25 layer the ratio of  $\text{H}_2/\text{Ar}$  was much larger than one and  
26 the total pressure was larger than 20 mTorr. Both of  
27 these conditions were found to be necessary for the  
28 deposition of partially crystallized N-layer. The  
29 polycrystalline undoped silicon target, 5" in di-  
30 ameter, was supplied with an RF power of 100 watts  
31 leading to a target voltage of -1200 volts. The depo-  
32 sition lasted for 6 min. leading to a film of approxi-

1 mately 200 Å thick. As mentioned earlier this film has  
2 a conductivity of about  $10 (\Omega \text{ cm})^{-1}$  and is far more  
3 transparent than the corresponding amorphous N-layer.

4 At this point the substrate with the N-layer  
5 was transferred in another clean chamber for the depo-  
6 sition of the intrinsic I-layer. This layer was depo-  
7 sited in an atmosphere of 5 mTorr of Ar + H<sub>2</sub>. The  
8 hydrogen content in this discharge was approximately  
9 18% of the argon content. The 5" polycrystalline  
10 undoped silicon target was supplied with an RF power  
11 of 80 watts leading to a bias voltage of -1000 volts.  
12 The deposition for this layer lasted 60 min. leading  
13 to an I-layer about 4000 Å thick. The substrate  
14 temperature during this deposition was maintained at  
15 325°C.

16 The partially crystallized P-layer was depo-  
17 sited next in an atmosphere of 40 mTorr of H<sub>2</sub> + Ar +  
18 B<sub>2</sub>H<sub>6</sub>. The partial pressures of these gases were 36  
19 mTorr of hydrogen and 4 mTorr of argon. The B<sub>2</sub>H<sub>6</sub> was  
20 contained in the cylinder of argon at a concentration  
21 of 0.2 atomic %. Under these conditions the P-layer is  
22 partially crystallized having a conductivity of about  
23  $2 (\Omega \text{ cm})^{-1}$  and high transparency. The polycrystalline  
24 undoped silicon target, 5" in diameter, was supplied  
25 with an RF power of 60 watts, leading to a target  
26 voltage of -800 volts. The deposition of this layer  
27 lasted for 3 min., leading to a P-layer of 100 Å  
28 thickness.

29 At this point the substrate with the three  
30 active layers (N,I,P) was moved to another sputtering  
31 chamber for the deposition of an ITO (Indium Tin  
32 Oxide) layer on the top of the P-layer. This layer was  
33 deposited from an ITO target in an atmosphere of

0139487

- 13 -

1 argon. The target voltage during this deposition was  
2 maintained at -600 volts and the thickness of this  
3 layer was chosen to be 600 to 700 Å. A metal grid  
4 made of silver was deposited on the top of the ITO.

- 13 -

## CLAIMS:

- 1           1. A method for producing an amorphous silicon  
2 PIN or NIP semi-conductor device having partially crystal-  
3 lized (microcrystalline) P and N-layers comprising:
- 4           providing a substrate having at least a surface  
5 region comprising an electroconductive material which  
6 forms an ohmic contact to doped microcrystalline sili-  
7 con;
- 8           reactively sputtering a layer of microcrystal-  
9 line silicon doped with one type of charge carrier  
10 onto at least said surface region of the substrate;
- 11          reactively sputtering a layer of amorphous  
12 intrinsic, I, silicon onto said layer of silicon doped  
13 with said one type of charge carrier;
- 14          reactively sputtering a layer of microcrystal-  
15 line silicon doped with the other type of charge  
16 carrier onto said I layer;
- 17          sputtering an electroconductive material onto at  
18 least a region of said layer of microcrystalline sili-  
19 con doped with said other type of charge carrier which  
20 material forms an ohmic contact thereto.
- 21          2. A method according to claim 1 wherein said one type  
22 of charge carrier is N type and said other type of  
23 charge carrier is P type.
- 24          3. A method according to claim 1 wherein said one type  
25 of charge carrier is P type and said other type of  
26 charge carrier is N type.

1     4. A method according to either of claims 2 and 3 wherein said reac-  
2     tive sputtering of N doped microcrystalline silicon  
3     comprises sputtering microcrystalline silicon in par-  
4     tial pressures of hydrogen, ranging from about 20  
5     mTorr to about 80 mTorr, and argon ranging from about  
6     3 mTorr to about 10 mTorr, said partial pressure of  
7     argon including about 0.2 to 1 atomic % of phosphine  
8     (PH<sub>3</sub>).

9     5. A method according to claim 4 wherein said N-doped  
10    microcrystalline silicon is sputtered from an undoped  
11    polycrystalline silicon target.

12    6. A method according to any one of the preceding claims wherein  
13    an RF sputtering power of about 100 watts to 200 watts is coupled  
14    to the plasma, resulting in a target dc voltage of  
15    about -800 volts to about -2000 volts.

16    7. A method according to claim 6 wherein said substrates  
17    are maintained at a temperature ranging from about  
18    200°C to about 400°C.

19    8. A method according to any one of the preceding claims wherein  
20    said reactive sputtering of the intrinsic, I, layer of silicon  
21    comprises sputtering silicon in partial pressures of  
22    hydrogen, ranging from about 0.3 mTorr to about  
23    1.5 mTorr, and argon, ranging from about 3 mTorr to  
24    about 15 mTorr.

25    9. A method according to any one of claims 2 to 8 wherein said reac-  
26    tive sputtering of the P layer of microcrystalline  
27    silicon comprises sputtering microcrystalline silicon  
28    in partial pressures of hydrogen, ranging from about  
29    20 mTorr to about 80 mTorr, and argon, ranging from  
30    about 3 mTorr to about 10 mTorr, said argon containing  
31    about 0.2 to 1 atomic % of diborane, B<sub>2</sub>H<sub>6</sub>.



10. A method according to any one of the preceding claims wherein said electroconductive material, sputtered onto said P-doped microcrystalline silicon is a thin film of material selected from indium tin oxide, tin oxide and cadmium stannate.

5

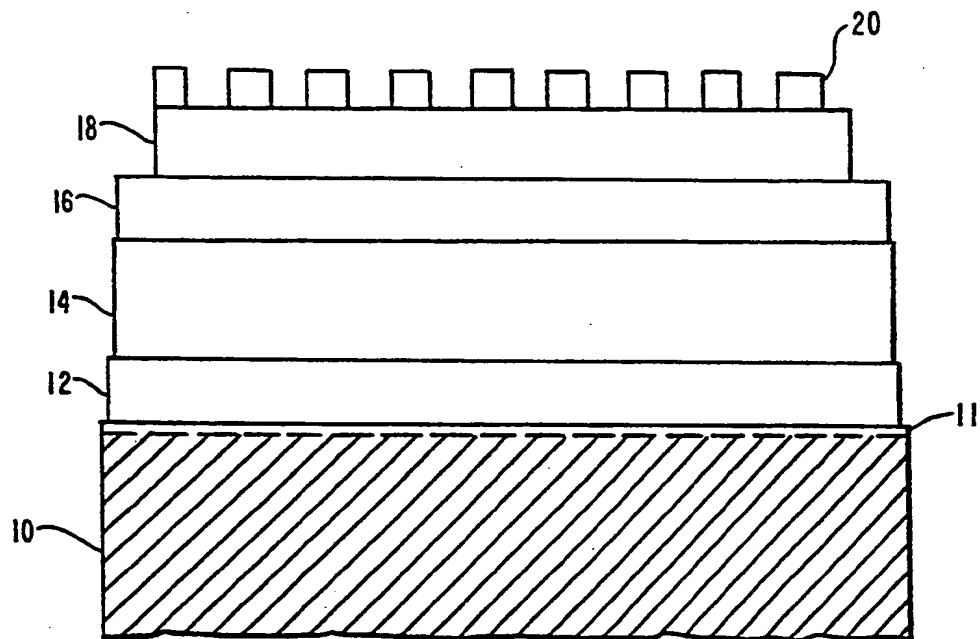


FIG. I

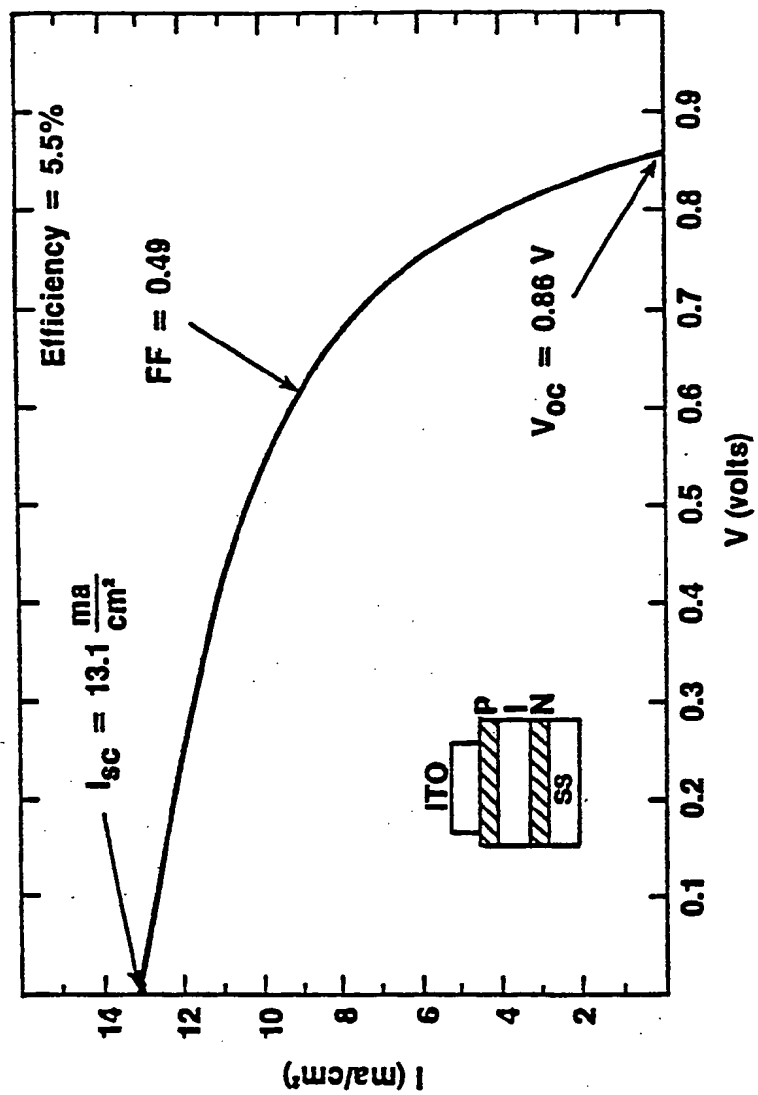


FIG. 2

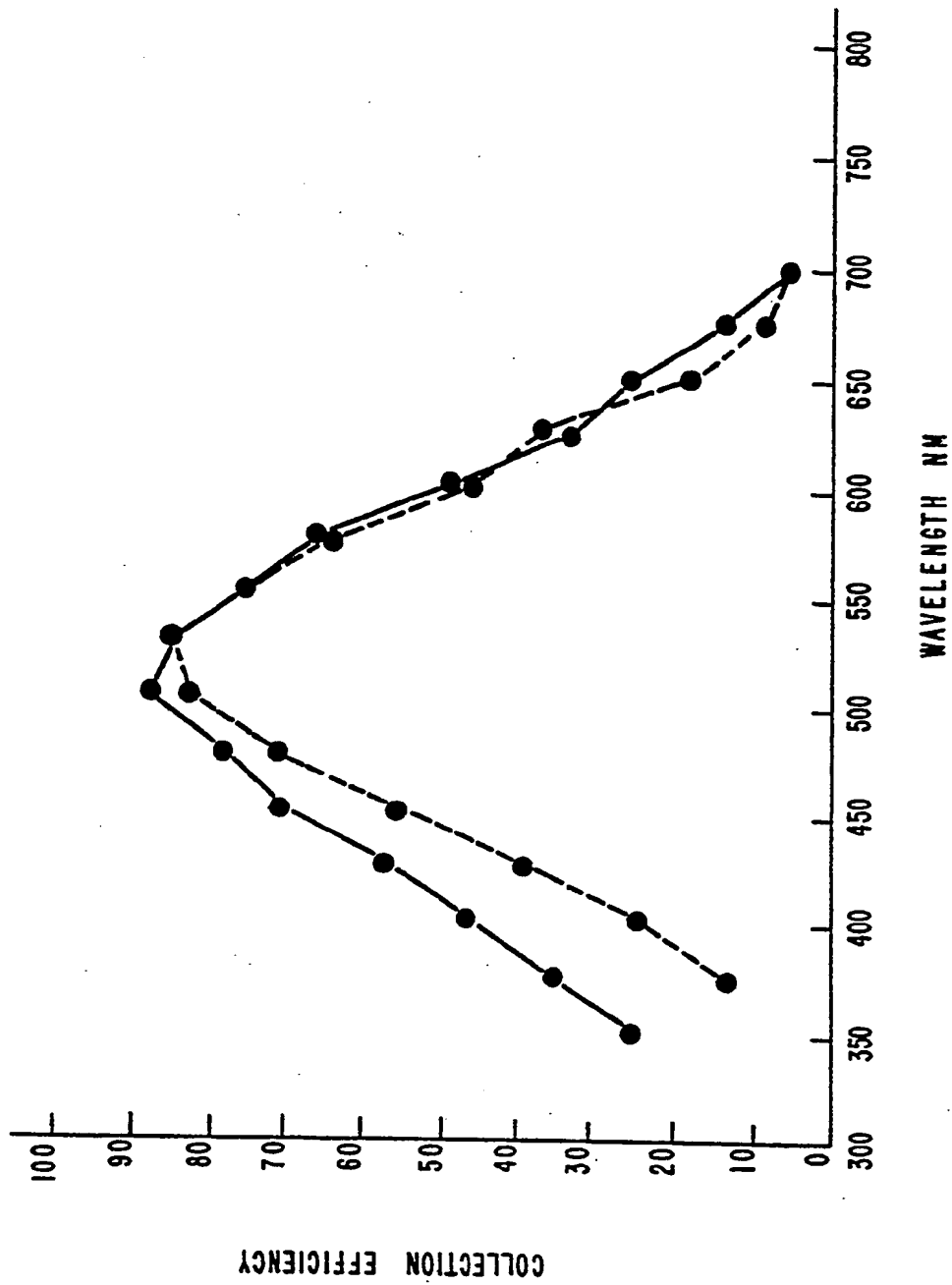


FIG. 3



European Patent  
Office

# EUROPEAN SEARCH REPORT

0139487

Application number

EP 84 30 6505

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Y	DE-A-3 119 631 (MESSERSCHMITT-BÖLKOW-BLOHM) * Claims 1-7 *	1-3	H 01 L 21/203 H 01 L 31/18
Y	EP-A-O 060 363 (EXXON) * Claims 1-3, 6, 7 *	1-3, 7 8, 10	
A	WO-A-8 101 914 (J. GIBBONS) * Claim 1 *	1-3	
Y	IBM TECHNICAL DISCLOSURE BULLETIN vol. 19, no. 12, May 1977, New York, USA; H. BRODSKY et al. "Doping of sputtered amorphous semiconductors" * Pages 4802-4803 *	4, 5, 8 9	
A	JAPANESE JOURNAL OF APPLIED PHYSICS vol. 21, no. 4, part 2, April 1982, Tokyo, JP; M. NODA et al. "Microstructures and hydrogen bonding environments of sputter-deposited a-Si:H films" * Pages L 195-197 *		TECHNICAL FIELDS SEARCHED (Int. Cl. 4)  H 01 L 21/203 H 01 L 31/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 18-12-1984	Examiner ROTHER A H J
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



European Patent  
Office

# EUROPEAN SEARCH REPORT

0139487

Application number

EP 84 30 6505

Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, A	JAPANESE JOURNAL OF APPLIED PHYSICS vol. 21, no. 9, part 2, September 1982, Tokyo, JP; Y. UCHIDA et al. "Microcrystalline Si:H Film and its application to solar cells" * Pages L 586-588 *  -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 18-12-1984	Examiner ROTHER A H J
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons  & : member of the same patent family, corresponding document	